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Perturbation Theory and Spin-Coupling Constants in Substituted Compounds. Ligands with Valence *ns* Orbitals

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An analytical perturbation extension of the Pople–Santry theory of the Fermi contact term in reduced spin-coupling constants ${}^1K$(E–L) has been developed for the substituted compounds $EL_{m-k}L'_k$ (E is a transition metal, M, or main-group element, A) where the ligands L have a valence *ns* orbital. The difference in ligand σ-orbital energies, $\delta\alpha' = \alpha(L') - \alpha(L)$, was taken as a perturbation. It was found that changes in ${}^1K$(E–L) under substitution should typically follow changes in the s contributions to the E–L bond-overlap population, the latter having been determined earlier for the various polyhedra $EL_{m-k}L'_k$. The obtained results agree with experiment and permit the known regularities of ${}^1K$(E–L) to be explained and a number of predictions to be made.

Introduction

At present, NMR spectroscopy is one of the most widespread methods for studying different chemical problems.[1,2] As the efficiency and informativity of any experimental technique is eventually determined by the accuracy of its theory, much effort has been devoted to developing the theories of NMR chemical shifts and reduced spin-coupling constants, K(E–L).[1,2] As K(E–L) values are not very sensitive to external factors such as temperature, solvents, etc., they can be considered as intrinsic characteristics of the E–L interactions, especially for directly bonded atoms E and L in various EL_m compounds (E is a transition metal, M, or main-group element, A). The general theory of ${}^1K$(E–L) is extremely complicated,[3] and, in fact, there exists only one analytical version of this theory which is of general chemical importance, namely, the Pople–Santry (P–S) theory,[4] which is based on the LCAO MO approximation. Although all three possible contributions to ${}^1K$(E–L), namely, the Fermi contact (FC), orbital, and spin-dipolar terms, are included, the interpretation of ${}^1K$(E–L) is usually reduced to a consideration of the FC term which is typically dominant[1,2] and analytically the simplest.[3,4] The major restriction of the P–S theory,[4] however, is that very elegant and simple expression (of the FC term only) applies just to unsubstituted EL_m compounds where all ligands must be geometrically equivalent. It is not quite obvious how to apply the P–S theory to ${}^1K$(E–L) in various substituted $EL_{m-k}L'_k$ compounds with different geometries and different E, L, L′, and k.

As the FC term in ${}^1K$(E–L) is eventually determined by the s-orbital interactions, it is reasonable to connect changes in ${}^1K$(E–L) under substitution, $EL_m \rightarrow EL_{m-k}L'_k$ with changes in the s_E–s_L contributions to the σ E–L bond. One must, however, distinguish ligands L with valence *ns* orbitals (H, CH_3, PR_3, etc.) from L with a low lone ns^2 pair (F) because the FC mechanisms will be quite different for each case.[4] Recently we have developed a general perturbation approach to the effects of substitution in various σ-bonded $EL_{m-k}L'_k$ compounds permitting changes in the valence s (as well as p and d) contributions to the E–L bond-overlap populations to be obtained in explicit form.[5-7] Our perturbation approach may be used to modify the P–S theory to make it applicable to substituted $EL_{m-k}L'_k$ compounds. In the present paper we will develop the theory of ${}^1K$(E–L) for ligands L with valence *ns* orbitals, a straightforward matter for our perturbation formalism.[5-7] The theory of spin-coupling constants in various fluorides, requiring some extension of our formalism, will be given elsewhere.[8]

Results and Discussion

General Relationships. In the framework of the P–S theory the FC term will be[4] given by eq 1. Here $\pi_{s_Es_L} = \pi_{\mu\nu}$ is a

$$ {}^1K(\text{E–L}) = |\text{const}|\cdot\pi_{s_Es_L} \tag{1}$$

mutual polarizability of the orbitals. $s_E = \mu$ and $s_L = \nu$ in eq

$$\pi_{\mu\nu} = 4\sum_i^{\text{occ}}\sum_j^{\text{unocc}}(\epsilon_i - \epsilon_j)^{-1}c_{i\mu}c_{i\nu}c_{j\mu}c_{j\nu} \tag{2}$$

2 where the indices i and j refer to the occupied and unoccupied canonical LCAO MO's of the compound in question. For ligands L with valence *ns* orbitals, the σ_L orbitals are either pure s ones (for instance, 1s for H) or some hybrids

$$\sigma_L = c_s s_L + c_p p_L \tag{3}$$

with valence s contributions.

Expressions 1 and 2 can be substantially simplified for the special case of EL_m compounds where, first, *all* ligands, L, are geometrically equivalent, and, second, *only one* central atom orbital, s_E, belongs to the totally symmetric (A_1) irreducible representation. In this case,[4] there will be only two MO's of A_1 symmetry which contribute to ${}^1K$(E–L), namely, bonding ϕ_1 (4) and antibonding $\phi_1{}^*$ (5). Taking into account (3), $\pi_{\mu\nu}$

$$\phi_1 = as_E + b(1/m^{1/2})(\sigma_1 + \sigma_2 + ... + \sigma_m) \tag{4}$$

$$\phi_1{}^* = bs_E - a(1/m^{1/2})(\sigma_1 + \sigma_2 + ... + \sigma_m) \tag{5}$$

(2) is reduced to (6) so that for such EL_m compounds we have

$$\pi_{s_Es_L} = \frac{1}{\epsilon(\phi_1{}^*) - \epsilon(\phi_1)}\,\frac{4a^2b^2c_s{}^2}{m} > 0 \tag{6}$$

(7) which is always positive and proportional to the square of

$${}^1K(\text{E–L}) = |\text{const}'|\cdot P_{s_Es_L}{}^2 \tag{7}$$

the E–L s bond order, $P_{s_Es_L}$ (cf. ref 4).

If all ligands L are not geometrically equivalent (for instance, in trigonal-bipyramidal EL_5, D_{3h} complexes) or more than one central atom orbital belongs to the totally symmetric

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Table I. Changes in the Bond Properties in Some $EL_{m-k}L'_k$ Compounds with Equivalent E-L Bonds[a]

compd	property[b]	sign of changes[b]	dependence on k
linear ELL′	$\delta K(E-L)/\delta\alpha'$	–	
	$\delta N(E-L)/\delta\alpha'$	–[c]	
planar trigonal	$\delta K(A-L)/\delta\alpha'$	–	monotonic
$AL_{3-k}L'_k$	$\delta N(A-L)/\delta\alpha'$	–[c]	monotonic
tetrahedral	$\delta K(A-L)/\delta\alpha'$	–	monotonic
$AL_{4-k}L'_k$	$\delta N(A-L)/\delta\alpha'$	–	monotonic

[a] $m = 2, 3, 4$; $k = 1, 2, \cdots, m - 1$. [b] The signs of $\delta K(E-L)/\delta\alpha'$ and $\delta N(E-L)/\delta\alpha'$ correspond to those of the s and total (s + p + d) contributions to $\delta N(E-L)/\delta\alpha'$, respectively.[5-7] [c] In some exceptional cases the positive sign is not excluded.[5]

representation (for instance, in trigonal-pyramidal compounds like NH_3 C_{3v}), the values of ${}^1K(E-L)$ should be determined from the general relationship (1). Certainly, if the mean excitation energy approximation is made, replacing all $\Delta\epsilon_{ij} = \epsilon_i - \epsilon_j$ by an average value $\Delta\epsilon$, (1) will be reduced to (7)[4] but this approximation should be analyzed for every concrete case.

Difficulties increase much more upon going from EL_m to substituted derivatives, $EL_{m-k}L'_k$, because changes in ${}^1K(E-L)$ are determined by changes in the relevant values of $\pi_{s_Es_L}$ (2). If we accept the difference in ligand σ-orbital energies $\delta\alpha'$ (8)

$$\delta\alpha' = \langle\sigma_{L'}|H|\sigma_{L'}\rangle - \langle\sigma_L|H|\sigma_L\rangle \tag{8}$$

as a perturbation, the changes in ${}^1K(E-L)$ can be expressed in terms of $\delta\pi_{s_Es_L}/\delta\alpha'$. In the general case of the monosubstituted compound $EL_{m-1}L'$ we have, to first order, eq 9. Here

$$\frac{\delta\pi_{s_Es_L}}{\delta\alpha'}\left[\frac{m}{4a^2b^2c_s^2}\right] = -\frac{1}{\epsilon_{i+1}-\epsilon_1}\left[\sum_{\substack{k=2\\(k\neq i+1)}}^{i+j}\frac{c_{kL'}c_{kL}}{\epsilon_k-\epsilon_1} + \sum_{\substack{k=2\\(k\neq i+1)}}^{i+j}\frac{c_{kL'}c_{kL}}{\epsilon_k-\epsilon_{i+1}} + \frac{2(a^2-b^2)}{m(\epsilon_{i+1}-\epsilon_1)}\right] + (\epsilon_{i+1}-\epsilon_1)\left[\sum_{k=2}^{i,\mathrm{occ}}\frac{c_{kL'}c_{kL}}{(\epsilon_k-\epsilon_1)(\epsilon_k-\epsilon_{i+1})^2} + \sum_{k=i+2}^{i+j,\mathrm{unocc}}\frac{c_{kL'}c_{kL}}{(\epsilon_k-\epsilon_1)^2(\epsilon_k-\epsilon_{i+1})}\right] \tag{9}$$

all coefficients refer to the relevant unperturbed LCAO MO's of EL_m where, regardless of geometry, we can always obtain the MO's of the (4) and (5) type.[5-7] The MO's $\phi_1, \phi_2, ..., \phi_i$ are occupied, and $\phi_{i+1}, \phi_{i+2}, ..., \phi_j$ are unoccupied.

Certainly, if ${}^1K(E-L)$ can be reduced to (7), both the signs and relative values of $\delta K(E-L)/\delta\alpha' = |\mathrm{const}|\delta\pi_{s_Es_L}/\delta\alpha'$ [cf. (1)] will coincide with those of $\delta P_{s_Es_L}/\delta\alpha'$ [cf. (7)] or of the s contribution, $\delta N_{s_Es_L}/\delta\alpha'$, to $\delta N(E-L)/\delta\alpha'$ where $N(E-L)$ is the E–L bond-overlap population [cf. (3)]. Though in the general case (9) changes in ${}^1K(E-L)/\delta\alpha'$ are rather complicated, one can show[9] that, typically, they also follow changes in $\delta N_{s_Es_L}/\delta\alpha'$. The proof follows the same lines which were used earlier to find the signs and relative values of $\delta N(E-L)/\delta\alpha'$.[5-7] We will illustrate it by one example concerning the tetrahedral compounds AL_3L'. In this case the general expression (9) will be given by (10) which is rather similar to the relevant expression for $\delta N(A-L)/\delta\alpha'$ (see eq 35 in ref 5 where the definitions of all coefficients, a, b, e, and f, and energies, E_{12}, E_{13}, etc., appear).

$$\frac{\delta\pi_{s_As_L}}{\delta\alpha'}\left[\frac{4}{a^2b^2c_s^2}\right] = -\frac{1}{E_{13}}\left[\frac{f^2}{E_{23}} - \frac{f^2}{E_{12}} + \frac{e^2}{E_{34}} - \frac{e^2}{E_{14}} + \frac{2(a^2-b^2)}{E_{13}}\right] - E_{13}\left[\frac{f^2}{E_{12}E_{23}^2} + \frac{e_2}{E_{14}^2E_{34}}\right] < 0 \tag{10}$$

So, we can transfer our results concerning the s contribution in $\delta N(E-L)/\delta\alpha'$[5-7] to $\delta\pi_{s_Es_L}/\delta\alpha'$ as given in Tables I and II. Remembering that $\delta\alpha' > 0$ corresponds to a better donor, L′, but $\delta\alpha' < 0$ to a better acceptor, L′, we can draw the following conclusions from Tables I and II.

Main Conclusions. (1) In linear ELL′, planar-trigonal $AL_{3-k}L'_k$, and tetrahedral $AL_{4-k}L'_k$ compounds the values of ${}^1K(E-L)$ should decrease for a better donor substituent, L′, but increase for a better acceptor, L′, changing monotonically as k increases. A great deal of experimental data (see, for instance, the reviews[1,2] and references therein) confirms these conclusions. Some examples are given in Table III. Let us stress that these experimental data have usually been explained, except for direct computations, by semiempirical arguments, e.g., Bent's rules,[10] but Bent's rules themselves have only been justified and represented in explicit analytical form for the first time in ref 5.

In principle, changes in ${}^1K(A-L)$ should be proportional to the electronegativity difference between L and a substituent L′.[5] Contributions to ${}^1K(A-L)$ other than the FC term may mean, however, that the order of a series of substituents on the basis of changes in coupling constant will depend strongly on the nature of A and L. For instance, the L′ series for

Table II. Signs of Changes in the Bond Properties in Some $EL_{m-k}L'_k$ Compounds with Nonequivalent E-L Bonds

compd			bond	
parent	substituted	property[a]	$E-L_{tr}$	$E-L(L'')_{cis}$
d^8 ML_4 D_{4h}	ML_3L' C_{2v}, $MLL'L''_2$ C_{2v}			
d^0-d^8 ML_5 D_{3h}	ML_4L' C_{3v}	$\delta K(M-L)/\delta\alpha'$	–	+[b]
d^0-d^6 ML_6 O_h	ML_5L' C_{4v}, $ML_3L'L''_2$ C_{2v}	$\delta N(M-L)/\delta\alpha'$	–	±δ[c]
d^0-d^4 ML_7 D_{5h}	ML_6L' C_{5v}			
d^0-d^8 ML_5 D_{3h}	ML_4L' C_{2v}	$\delta K(M-L)/\delta\alpha'$	*d*	+[b]
d^0-d^4 ML_7 D_{5h}	ML_6L' C_{2v}	$\delta N(M-L)/\delta\alpha'$		±δ[c]
12e AL_4 D_{4h}	AL_3L' C_{2v}, $ALL'L''_2$ C_{2v}	$\delta K(A-L)/\delta\alpha'$	–	none
14e AL_6 O_h	AL_5L' C_{4v}, $AL_3L'L''_2$ C_{2v}	$\delta N(A-L)/\delta\alpha'$	–	none
10e AL_5 D_{3h}	AL_4L' C_{3v}, $AL_3L'_2$ D_{3h}[e]	$\delta K(A-L)/\delta\alpha'$	+[b]	–
12e AL_6 O_h	AL_5L' C_{4v}, $AL_3L'L''_2$ C_{2v}	$\delta N(A-L)/\delta\alpha'$	±	–
14e AL_7 D_{5h}	AL_6L' C_{5v}, $AL_5L'_2$ D_{5h}[e]			
10e AL_5 D_{3h}	AL_4L' C_{2v}, $AL_3L'_2$ C_{2v}	$\delta K(A-L)/\delta\alpha'$	*d*	–
14e AL_7 D_{5h}	AL_6L' C_{2v}	$\delta N(A-L)/\delta\alpha'$		–

[a] See footnote *b* to Table I. [b] The opposite sign is not excluded. [c] The effect is relatively small in absolute value and may be of any sign. [d] The influence of the equatorial substituent L′ on other equatorial ligands depends on the value of the relevant valence angle. See details in ref 7. [e] In the $AL_3L'_2$ and $AL_2L'_3$ D_{3h} complexes there exist only the $A-L_{cis}$ bonds, $A-L_{eq}$ and $A-L_{ax}$, respectively. The same holds for the $AL_5L'_2$ and $AL_2L'_5$ D_{5h} complexes.

Table III. Experimental Values of ^1J(A–H), Hz, in Some Tetrahedral $AH_{4-k}L'_k$ Compounds[a, b]

L′	H	F	Cl	Br	I	OCH_3
CH_3L'	125	149	150	152	151	140
$CH_2L'_2$	125	185	178	179	173	162
CHL'_3	125	238	209	206		186
SiH_3L'	202.5	229.0	238.1	240.5	240.1	
$SiH_2L'_2$	202.5	282.0	288.0	289.0	280.5	
$SiHL'_3$	202.5	381.7	362.9			

[a] All data were taken from ref 11. [b] The absolute values of ^1J(Si–H) < 0 are given because ^1K(Si–H) > 0.

^1J(A–H) in $AH_{4-k}L'_k$ compounds is not exactly the same even for A = C and Si (see Table III). It is very interesting to note that in $(CH_3)_3SiL'$ the values of $|^1J(\text{Si–C})|$ decrease along the "ideal" L′ series, namely, for L′ = F, OR, Cl, $NHSi(CH_3)_3$, Br, I, Ph, CH_3, H, and $Si(CH_3)_3$ they are 60.5, 59.0–60.0, 57.7, 56.2, 56.0, 54.0, 52.2, 51.0, 50.8, and 43.6 Hz, respectively.[12] One can add that the regularities of ^1J(C–C)[13] and ^1J(Si–C) are strikingly similar, so that "the same mechanism is operative for (C,C) and (Si,C) coupling, and the silicon d orbitals do not participate to any great extent in the Si–C bonding".[12] From the general references,[1,2] it is worth mentioning the reviews of spin-coupling constants of ^{13}C with various first-row nuclei[13] and of ^{31}P with various transition-metal and main-group atoms.[14,15]

Because the signs of δK(E–L) and δN(E–L) should be typically the same for a given L′, we can anticipate that an increase in δK(E–L) will correspond to an increase in the E–L bond strength (a decrease in the E–L bond length) and vice versa for a decrease in δK(E–L). Excepting cases involving serious steric hindrances, for instance in some monosubstituted tetrahedral AL_3L' compounds (see the discussion in ref 5), this is what one observes.[1,2]

(2) For the $M\text{–}L_{tr}$ bonds (tr = trans) in transition-metal complexes, $ML_{m-1}L'$, m = 4–7 (and related $ML_{m-k-1}L''_kL'$), and for a given substituent L′, the signs of $\delta K(M\text{–}L_{tr})$ and $\delta N(M\text{–}L_{tr})$ are the same, positive for a better donor L′ and negative for a better acceptor L′. Changes in $^1K(M\text{–}L_{tr})$ should be, in principle, proportional to the difference in electronegativity of L vs. L′ though here, as we mentioned above, the L′ series may depend on the nature of M and L. As a whole, these facts explain the well-known correlations of spin–spin coupling constant vs. bond length which represent the main manifestations of the trans influence regularities in transition-metal chemistry (see ref 15–18 for instance, and references therein). By the way, from Tables I and II it follows that the regularities of trans influence should be the same for linear ELL′ and various transition-metal $ML_{m-1}L'$ complexes. Indeed, the L′ series for, say, $^1K(M\text{–}^{31}P)$ is practically the same for linear $L'\text{–}Hg^{II}\text{–}PR_3$ and square $L'\text{–}Pt^{II}L_2(PR_3)$ compounds.[16]

For the $M\text{–}L_{cis}$ bonds, on the other hand, it follows from Table II that there is no *definite* correspondence between the signs of $\delta K(M\text{–}L_{cis})$ and $\delta N(M\text{–}L_{cis})$. We can anticipate, then, that there can be no *general* correlations $^1K(M\text{–}L_{cis})$ vs. $R(M\text{–}L_{cis})$ and, in fact, none have been found experimentally.[15–18]

(3) For square AL_4 and octahedral AL_6 main-group complexes where A is not of the highest oxidation state, we can predict the insensitivity of $^1K(A\text{–}L_{cis})$ to substitution, but for the trans bonds we should have the same regularities of trans influence as for transition-metal complexes. Unfortunately, we failed to find the relevant experimental data to check this prediction.

(4) For trigonal AL_5 and pentagonal AL_7 bipyramidal as well as for octahedral AL_6 main-group complexes (where A is of the highest oxidation state), the $A\text{–}L_{cis}$ bonds, the $A\text{–}L_{eq}$ ones under axial substitution and the $A\text{–}L_{ax}$ ones under equatorial substitution should show the same regularities in $^1K(A\text{–}L_{cis})$ as the $M\text{–}L_{tr}$ bonds in transition-metal complexes. At the same time one cannot expect any definite regularities of $^1K(A\text{–}L_{tr(ax)})$ under axial substitution for all $AL_{m-1}L'$ complexes and of $^1K(A\text{–}L_{eq})$ under equatorial substitution for AL_5 and AL_7 complexes. The known experimental data (unfortunately, very scarce and mainly for $PL_{5-k}L'_k$ and $PL_{6-k}L'_k$[14,15]) agree with these conclusions. For instance, upon going from HPF_4 to H_2PF_3, where atoms H occupy equatorial positions and the s character and strength of the P–H bonds decrease,[6,7] the values of ^1K(P–H) also decrease, being 1075 and 841 Hz, respectively.[14]

Comparison with Other Approaches. To our knowledge, there have been only two attempts[19,20] to apply a perturbation theory for similar purposes, both for ^1K(C–H) and ^1K(Si–H) in the relevant tetrahedral series $AH_{4-k}L'_k$, k = 0–3. Though the Vladimiroff–Malinovski approach[19] was based on a first-order perturbation theory, the authors made no specific identification of the nature of the perturbation. The Ditchfield–Jensen–Murrell (DJM) approach[20] is rather similar to ours in taking only the FC term and $\delta\alpha'$ (8) as a main perturbation. However, unlike our analytical procedure, the DJM one was "to set up a calculation of $\pi_{\mu\nu}$ for the parent molecules CH_4 and SiH_4 and then to vary the parameters *numerically* (E.SH.) in such a way that a Taylor expansion in terms of these parameters can be derived".[20a] It is noteworthy that sets of parameters which gave exact values for ^1J(A–H) in AH_4 are rather specific, for instance, $\alpha(s_c)$ = −16.00 eV[20] instead of the usual value of −21.4 eV.[21]

Concluding Remarks

The developed model represents a perturbation extension of the P–S theory[4] of the FC term in ^1K(E–L) for various substituted compounds, $EL_{m-k}L'_k$, where L has a valence *ns* orbital. In these cases, the sign of ^1K(E–L) in parent EL_m compounds is positive and changes in ^1K(E–L) under substitution should typically follow those in the s contribution to N(E–L). For this reason only, the s character of the E–L bond can be correlated with the values of ^1K(E–L) and sometimes with the E–L bond strength (length). From our model it follows (see Tables I and II) that the correlations $\%s_E$ vs. ^1K(E–L) vs. R(E–L) are reliable in some cases (first of all, for the $M\text{–}L_{tr}$ bonds) but not others (for instance, for the $M\text{–}L_{cis}$ bonds).

For main-group element compounds, $AL_{m-k}L'_k$, all the substitution effects depend strongly on the oxidation state of the central atom.[6,7] In the present work we have considered $AL_{m-k}L'_k$ compounds where A is of the highest oxidation state or if not, A is in square or octahedral environments which corresponds to the MO scheme (4) and (5) and therefore to positive values of ^1K(A–L) according to (7). It is another story, however, for compounds like angular SeL_2 or trigonal-pyramidal PL_3 where the central atoms are not of the highest oxidation state, and, moreover, the A–L bonds are formed mainly at the expense of the p_A orbitals with the s_A orbital forming the main part of a lone pair. The perturbation treatment of such compounds shows[22] that the effects of substitution may be both similar and different from those for linear ALL′ and planar-trigonal $AL_{3-k}L'_k$ compounds, respectively,[5,8] where A is of the highest oxidation state. In particular, the general expression (1) can result in both positive and negative values of ^1K(A–L), the former being typical for more electronegative L.[22] Indeed, all the known values of ^1K(P–H) and ^1K(Se–H) are positive, but in some compounds the values of ^1K(P–C) have been found to be both positive and negative and ^1K(Se–C) negative (see a discussion in ref 13, 14, 23). This reversal of the sign has been explained[23] by the contribution of "the indirect FC term". In our model[22] this reversal is caused mainly by the contribution of the lone pair having predominantly the s_A character. Such a mechanism is rather similar to that which results in the *negative* values of the FC term in ^1K(A–F) due to the presence of a fluorine lone $2s^2$ pair.[4,7,8] All these aspects will be discussed in detail elsewhere.[22]

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Crystal and Molecular Structure of μ-Peroxo-bis{[1,11-bis(2-pyridyl)-2,6,10-triazaundecane]cobalt(III)} Tetraiodide Trihydrate. A Cobalt Dioxygen Complex of a Pentadentate Ligand

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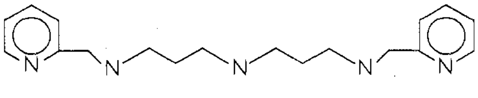
Single-crystal X-ray diffraction methods were employed to determine the structure of the reversible oxygen carrier μ-peroxo-bis{[1,11-bis(2-pyridyl)-2,6,10-triazaundecane]cobalt(III)} tetraiodide trihydrate, $[Co(PYDPT)]_2O_2I_4{\cdot}3H_2O$, $(CoN_5C_{18}H_{27})_2O_2I_4{\cdot}3H_2O$. The opaque crystals conform to the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 20.104$ (9) Å, $b = 11.896$ (5) Å, $c = 21.899$ (5) Å, and $\beta = 116.33$ (10)°; $Z = 4$. The observed density is 1.89 g cm^{-3} and the calculated density is 1.91 (1) g cm^{-3}. Least-squares refinement with omission of hydrogen atoms gave an R index of 7.0% for 4191 reflections with intensities greater than 4σ. The pyridyl nitrogens are cis to one another and to the dioxygen bridge in the distorted octahedral geometry around the cobalt atoms, so that an imine nitrogen is trans to the dioxygen bridge. The O–O distance of 1.456 (9) Å is consistent with the formulation of the dioxygen group as a peroxide (O_2^{2-}) ion and assignment of the tripositive oxidation state to the cobalt ions. The structure is compared with that of the analogous cobalt dioxygen complex containing disalicylaldehyde 3,3′-iminobis(propanimine) as a ligand for which the structure has been determined. The fact that the cobaltous complex of the analogous *N*-ethyl substituted ligand 1,11-bis(2-pyridyl)-6-ethyl-2,6,10-triazaundecane (PYEtDPT) does not react with molecular oxygen is attributed to steric hindrance at the oxygenation site.

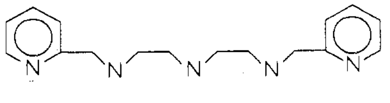
Introduction

In the course of recent studies of the chemistry of dioxygen complexes of transition metals,[1,2] X-ray analysis has provided information on the bonding of both mononuclear and dinuclear dioxygen complexes.[2] These dioxygen complexes are now formally represented by one or more oxidized metal ions bound to a superoxo or peroxo dioxygen group. Some of the dinuclear compounds for which structures are available are monobridged, with the metal centers bound only by the peroxo moiety,[3] while others have μ-amido[4] or μ-hydroxo[5] bridges in addition to the peroxo bridge. In aqueous solution, the formation of a μ-hydroxo bridge in addition to the μ-peroxo bridge has generally been observed when there is a free coordination site on each of the metal ions after oxygenation; this bridge apparently stabilizes the dioxygen complex.[6] The most elegant method for preventing formation of the second bridge is to employ pentadentate ligands, so that donor groups may occupy all of the coordination sites of the metal except for the site at which oxygenation occurs. The aqueous solution behavior and oxygenation of several cobalt(II) complexes with suitable pentacoordinate ligands have been reported.[7,8]

The complex chosen for study is of interest for several reasons: PYDPT (**1**) contains three amino and two pyridyl donor groups. These latter donors have the potential for π back-bonding, a process which should affect the π back-bonding, if any, to oxygen. It has been shown that π back-bonding from pyridyl groups to cobalt(II) enhances the stability of the ligand–cobalt bond.[7] The cobaltous complex of the ligand has the unusual ability to bind oxygen at low pH, but this is apparently due to formation of the metal–ligand complex in significant amounts at low pH rather than to



1 PYDPT



2 PYDIEN

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